

DTIC FILE COPY

4

David Taylor Research Center

Bethesda, Maryland 20884-5000

AD-A206 260

DTIC/SME-88/74 October 1988

Ship Materials Engineering Department
Interim Report

X-Ray Photoelectron Spectroscopy Study of Samples
in the Y-Ba-CuO System

by

L. F. Aprigliano

B. Friedman

R. J. Stockhausen

DTIC/SME-88/74 X-ray Photoelectron Spectroscopy Study of Samples
in the Y-Ba-CuO System

DTIC
ELECTE
S 3 APR 1989 D
E



Approved for public release; distribution
unlimited

89 4 03 032

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			
4 PERFORMING ORGANIZATION REPORT NUMBER(S)		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION David Taylor Research Center	6b OFFICE SYMBOL (If applicable) Code 2812	7a. NAME OF MONITORING ORGANIZATION	
6c ADDRESS (City, State, and ZIP Code) Bethesda, MD 20084-5000		7b ADDRESS (City, State, and ZIP Code)	
8a NAME OF FUNDING/SPONSORING ORGANIZATION David Taylor Research Center	8b OFFICE SYMBOL (If applicable) Code 0113	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c ADDRESS (City, State, and ZIP Code) Bethesda, MD 20084-5000		10 SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO 61152N	PROJECT NO TASK NO WORK UNIT ACCESSION NO ZR-000-01-01 DN508502
11 TITLE (Include Security Classification) (U) X-Ray Photoelectron Spectroscopy Study of Samples in the Y-Ba-Cu-O System			
12 PERSONAL AUTHOR(S) L.F. Aprigliano, B. Friedman, R.J. Stockhausen			
13a TYPE OF REPORT Interim	13b TIME COVERED FROM 7/87 TO 9/88	14 DATE OF REPORT (Year, Month, Day) 1988 Oct 31	15 PAGE COUNT 35
16 SUPPLEMENTARY NOTATION			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		X-ray Photoelectron Spectroscopy, Copper oxides, Superconductivity, Ceramics, Yttrium compounds, Barium compounds.	
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Superconducting ceramics that have critical temperatures which exceed the boiling point of liquid nitrogen (77 K) have been discovered. Preliminary studies both in the United States and Japan indicate that the superconducting properties of these ceramics can degrade with exposure to water vapor during processing. X-ray photoelectron spectroscopy (XPS) is a possible method with which to study this problem. The goal of this research was to determine if there are features in the XPS spectra of these ceramics that a spectrometer with non-monochromatic radiation can use to study this reaction. As the first step in this determination, it was necessary to ascertain the extent to which this method can discriminate between the ceramic superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$, and a poorly superconducting two phase sample, ($\text{YBa}_2\text{Cu}_3\text{O}_7$ and Y_2BaCuO_5). This latter sample results from processing errors when attempting to make single phase $\text{YBa}_2\text{Cu}_3\text{O}_7$. The core-level XPS spectra for these samples were acquired in this investigation. Differences in the spectra for the Y 3d			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/DUNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL L.F. Aprigliano		22b TELEPHONE (Include Area Code) (301) 267-2484	22c OFFICE SYMBOL Code 2812

19. ABSTRACT (Continued)

and O 1s peaks were found that might prove useful in distinguishing these two materials and studying the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with water. Core-level XPS spectra are being acquired for other stable phases in the Y-Ba-Cu-O system (such as BaCuO_2 , $\text{Y}_2\text{Cu}_2\text{O}_5$, and Y_2BaCuO_5) to continue building the basis from which the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with water can be studied.

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



CONTENTS

	Page
ABSTRACT	1
ADMINISTRATIVE INFORMATION	1
INTRODUCTION	2
BACKGROUND	2
PREVIOUS XPS WORK	3
EXPERIMENTAL PROCEDURE	12
SAMPLE PREPARATION	12
X-RAY PHOTOELECTRON SPECTROSCOPY	13
RESULTS AND DISCUSSION	16
SUMMARY	20
REFERENCES	31

FIGURES

1. Cu 2p _{3/2} peak synthesis using three gaussians for the superconducting sample	21
2. Cu 2p _{3/2} peak synthesis using two gaussians for the superconducting sample	22
3. Cu 2p _{3/2} peak synthesis using three gaussians for the "non-superconducting sample"	23
4. Y 3d peak synthesis using three gaussians for the superconducting sample	24
5. Y 3d peak synthesis using three gaussians for the "non-superconducting" sample	25

FIGURES (Continued)

6. Ba 3d _{5/2} peak synthesis using three gaussians for the superconducting sample	26
7. Ba 3d _{5/2} peak synthesis using three gaussians for the "non-superconducting" sample	27
8. O 1s peak synthesis using three gaussians for the superconducting sample	28
9. O 1s peak synthesis using three gaussians for the "non-superconducting" sample	29

ABSTRACT

Superconducting ceramics that have critical temperatures which exceed the boiling point of liquid nitrogen (77 K) have been discovered. Preliminary studies both in the United States and Japan indicate that the superconducting properties of these ceramics can degrade with exposure to water vapor during processing. X-ray photoelectron spectroscopy (XPS) is a possible method with which to study this problem. The goal of this research was to determine if there are features in the XPS spectra of these ceramics that a spectrometer with non-monochromatic radiation can use to study this reaction. As the first step in this determination, it was necessary to ascertain the extent to which this method can discriminate between the ceramic superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$, and a poorly superconducting two phase sample, ($\text{YBa}_2\text{Cu}_3\text{O}_7$ and Y_2BaCuO_5). This latter sample results from processing errors when attempting to make single phase $\text{YBa}_2\text{Cu}_3\text{O}_7$. The core-level XPS spectra for these samples were acquired in this investigation. Differences in the spectra for the Y 3d and O 1s peaks were found that might prove useful in distinguishing these two materials and studying the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with water. Core-level XPS spectra are being acquired for other stable phases in the Y-Ba-Cu-O system (such as BaCuO_2 , $\text{Y}_2\text{Cu}_2\text{O}_5$, and Y_2BaCuO_5) to continue building the basis from which the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with water can be studied.

ADMINISTRATIVE INFORMATION

This report was supported by the DTRC Independent Research Program, sponsored by the Office of Chief of Naval Research, Director of Navy Laboratories, OCNR 300, and administered by the Research Coordinator, DTRC 013, under program element 61152N, Task Area ZR-000-01-01 under DTRC Work Unit 1-2812-038. This work was supervised within the Metals and Welding Division (Code 281) by

Drs. J.P. Gudas and O.P. Arora. This report satisfies fiscal year 1988 milestone 1-2812-038-40.

INTRODUCTION

BACKGROUND

Superconducting ceramics that have critical temperatures which exceed the boiling point of liquid nitrogen (77 K) have been discovered.⁽¹⁾ The liquid nitrogen threshold temperature was first broken with $\text{YBa}_2\text{Cu}_3\text{O}_7$. This ceramic has a perovskite crystal structure that is oxygen deficient and has been speculated to have a high proportion of Cu in the +3 valence state. Preliminary studies, both in the United States and Japan, indicate that the superconducting properties of these ceramics can degrade with exposure to water vapor during processing. X-ray photoelectron spectroscopy (XPS) is a possible method with which to study this problem.⁽²⁾ The goal of this research is to determine if there are features in the XPS spectra of these ceramics that a spectrometer with non-monochromatic radiation can use to study this reaction.

PREVIOUS XPS WORK

The XPS spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other perovskite type ceramic superconductors have been reported to contain various features (oxygen peak splitting and Cu peak broadening) that can be associated with optimum and degraded superconducting properties. Ihara *et. al.*⁽³⁾, have obtained XPS spectra of $\text{Sr}_x\text{La}_{2-x}\text{CuO}_{4-y}$ where $x = 0.6$ and $y = 0.0$ before annealing and for $x = 0.6$ and $y = 0.9$ after annealing. From these spectra it is found that the core level $\text{Cu}2p_{3/2}$ peak becomes less broad upon annealing. This peak is deconvoluted into three sub-peaks having binding energies of 933.0, 934.3, and 935.7 electron volts (eV), with each peak having a full width at half maximum (FWHM) of 1.56 eV. These peaks are taken to originate from the monovalent, bivalent, and trivalent copper ions, respectively. The intensity of the Cu^{2+} peak is about double that of the Cu^{3+} and Cu^+ peaks⁽³⁾. Evidence for the existence of copper 3d holes is provided by the satellite peak located at about 943 eV⁽³⁾. This satellite peak originates from the electron transition of oxygen 2p states to copper 3d hole states, a consequence of photoelectron inelastic scattering.

The sharper $\text{Cu } 2p_{3/2}$ peak of the annealed sample comprises a predominant Cu^+ peak and a minor Cu^{2+} peak with binding energies of 933.1 eV and 934.7 eV, respectively, and an intensity ratio of 9:1.⁽³⁾ Weak satellite peaks are observed between the $\text{Cu } 2p_{3/2}$ peaks of the annealed sample. This data indicates that in the annealed sample, which was processed under the reducing conditions of

1.3×10^2 pascal (Pa) of oxygen atmosphere at 900°C for ten hours, the copper ions to a great extent are monovalent.

Ihara et. al.⁽³⁾, refer to a peak splitting of the oxygen 1s and 2s states which is supposed to relate to differing positions of oxygen in the unit cell of $\text{Sr}_x\text{La}_{2-x}\text{CuO}_{4-y}$. However, their 1s spectra is not published in their report and the published 2s spectra does not clearly show this splitting.

A more detailed study and analysis of an XPS spectra is given by Fujimori et. al.⁽⁴⁾. Their investigation deals with sintered and annealed samples of $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4-y}$ ($x = .25$ and $y = 0.1$) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$. A Mg K α -ray source was utilized. The core-level spectra of Fujimori et. al.⁽⁴⁾, have approximately the same binding energy range as the corresponding spectra of Ihara et. al.⁽³⁾. The main and satellite Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks correspond to the final state configuration $2p\ 3d^9$ and $2p\ 3d^{10}$ for the higher and lower binding energies, respectively, where $2p$ signifies the existence of a core hole. For each j -level ($j = 1/2, 3/2$) the main peak-satellite peak saturation is then estimated by the intra-atomic Coulomb energy between the 3d electron and the core hole. A further contribution to the satellite structure arises from a ligand-to-d charge transfer in the photoemission ground state.

Fujimori et. al.⁽⁴⁾, state that their XPS core spectra are then to

be interpreted as describing a ground state that is either a mixture of the d^9 and d^{10} configurations or only the d^9 configuration. It is deduced that the d^9 component in the ground state is not significant in all of the samples used for their core spectra and that the trivalent Cu is screened by a ligand-to-d charge transfer, becoming almost d^9 like in its ground state. Based upon this deduction, Fujimori et. al.⁽⁴⁾ assume that the copper sites are primarily divalent with the ground state being predominately d^9 . Their analysis is partly based upon the examination of the CuCl_2 XPS spectrum.

Jenny et. al.⁽⁵⁾, obtained core level XPS spectra for single-phase samples of $\text{La}_{1.5}\text{Ba}_{0.5}\text{CuO}_x$, $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Clean surfaces of the samples were prepared in flowing nitrogen with immediate transfer into the vacuum chamber. Previously appearing small shoulders at the oxygen level disappeared, although a small amount of carbon was still detected. Since the samples were not totally dense, the carbon was considered likely to be due to the absorption of carbon dioxide and carbon monoxide on the inner surfaces of the samples.

The copper $2p_{3/2}$ core level spectra (at approximately 933 eV) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were measured by Jenny et. al.,⁽⁵⁾ at $T = 77$ K and $T = 300$ K. No significant differences appear for the two temperatures. A satellite structure typical of paramagnetic copper ions is observed on the high binding energy side.

The barium 3d_{5/2} spectra for the sample was obtained for T = 77 K and T = 300 K.⁽⁵⁾ The main peak at about 780.5 eV, which is attributed to BaO, exhibits a shoulder at the lower binding energy side. This shoulder, which is generated by a minor peak, may be a product of the oxygen vacancies in the vicinity of the barium ions.

Dauth *et. al.*⁽⁶⁾, examined both unscrapped and clean specimens of YBa₂Cu₃O_{7-x} with aluminum K-radiation. The oxygen 1s core level spectra are exhibited only for room temperature for unscrapped and clean specimens. There is a significant difference between the unscrapped and clean conditions. In the clean condition a prominent peak is observed at about 528.5 eV. This peak is to a large extent masked (although not completely as stated by Dauth *et. al.*⁽⁶⁾) in the unscrapped conditions by a peak located at about 531 eV. This situation is considered by them to originate in contributions from both dimer and absorbed oxygen. They say that the oxygen 1s peak at 531 eV peak is not symmetric and that the asymmetry results from a further structure situated at about 533 eV. This structure is assumed to be due to the presence of O₂⁻² incipient dimers.

The copper 2p_{3/2} core-level spectra for YBa₂Cu₃O_{7-x} at 10 and 300 K are presented and compared to the CuCl₂ spectrum at an unstated temperature⁽⁶⁾. The peak structure situated between about 930 eV and 940 eV binding energy is attributed to the final state Cu d¹⁰-O 2p⁵. The peak structure located between about 940 eV and 945 eV is attributed to the Cu d⁹-O2p⁶ final state. The ground state

configuration is taken to be a linear combination of these two final states. There is no indication of any Cu d^9 -O p^6 final state.

The yttrium core-level $3d_{5/2}$ - $3d_{3/2}$ spin orbit doublet is presented for 10 and 300 K.⁽⁶⁾ There is no significant change in the peak shape between the two temperatures. In the region between 158 eV and 162 eV, it appears that there is some peak broadening in going from 300 to 10 K. Dauth *et. al.*⁽⁶⁾, claim to observe a narrowing of the peak in this binding energy region upon decreasing the specimen temperatures, but this is somewhat difficult to observe in the reported results.

Ramaker *et. al.*⁽⁷⁾, present XPS spectra for La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the tetrahedral (123-t) and orthorhombic (123-o) crystal structures using aluminum K-radiation. The core level spectra for these superconductors is presented along with the spectra for the reference materials Cu, Cu_2O , CuO, and La. Large satellites are observed in association with the copper $2p_{3/2}$ and $2p_{1/2}$ peaks for CuO but not for copper metal and Cu_2O .

Steiner *et. al.*⁽⁸⁾ determined the copper valence in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and in monovalent, divalent, and trivalent copper oxides from XPS core level spectroscopy. The Cu $2p_{3/2}$ spectra were measured by XPS for compounds in which the copper ion is in the nominal valent state of 0^+ (copper metal), 1^+ (Cu_2O), 2^+ (CuO), or 3^+ (NaCuO_2). The line width of the copper metal was found to be slightly smaller than that

of Cu_2O . The position of the Cu_2O peak is very close to that of the copper metal. The metal has the smallest line width of those measured. For the Cu^{3+} state of NaCuO_2 , the line is still narrow relative to the metal, although there is a shift of 2.25 eV to higher binding energies relative to Cu_2O . This shift upwards is in accord with the larger nominal ionic charge encountered in the Cu^{3+} compound. The divalent copper line has a width which is about twice that of the monovalent and trivalent copper lines. The trivalent state displays a very intense satellite while the Cu^+ and Cu^{3+} compounds have weak satellites.

Steiner et. al.⁽³⁾ present a spectrum of the Cu $2p_{3/2}$ lines of CuO , La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_7$, and NaCuO_2 . By comparing these spectra, the researchers deduce that a very large fraction of the copper ions in La_2CuO_4 , a base material for superconducting oxides, and in $\text{YBa}_2\text{Cu}_3\text{O}_7$, a superconducting oxide, are in the divalent state. This deduction is based upon the line positions, their almost equal widths, and the shape and intensity of the satellites.

In order to ascertain the presence of a trivalent copper contribution to the copper line intensity in the superconducting material, Steiner et. al.⁽³⁾ generated synthetic spectra from those for pure CuO and NaCuO_2 . These researchers concluded from the analysis of these spectra that there is probably no trivalent contribution greater than 5% in the spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Werfel et. al.⁽⁹⁾ studied the oxidation states of copper, barium and yttrium in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ using chromatized XPS core level measurements. Spectra for the $\text{Cu } 2p_{3/2}$ peak of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample is presented by Werfel et. al.⁽⁹⁾ along with the corresponding spectra of CuO and Cu_2O obtained under comparable experimental conditions. The estimated binding energy value of 933.1 eV is less than that of 933.5 eV for CuO but is larger than the binding energies of 932.7 eV and 932.4 eV for copper metal and Cu_2O , respectively. The $\text{Cu } 2p_{3/2}$ spectrum and the spectrum of Cu^{2+} in CuO display a similar satellite structure. The estimated FWHM value of 2.5 eV for the $\text{Cu } 2p_{3/2}$ line of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is less than the value of 3.2 eV obtained for CuO . The ratio of the intensity of the satellite structure on the high energy side to the peak intensity is 40% lower for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ than the corresponding ration for CuO . For both CuO and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ the satellite structure on the high energy side have the same energy position and width. Based on the results, Werfel et. al.⁽⁹⁾ deduce the existence of both monovalent and divalent copper in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

For the study of the structure of the barium $3d_{5/2}$ spectrum, Werfel et. al.⁽⁹⁾ examined the spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$, the latter having the regular perovskite structure. For both materials, the barium peaks exhibit an asymmetric low binding energy shoulder attributable to two differently charged barium ions. The lower binding energy component in the fit for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

specimen is deemed to originate from barium ions in almost perfect oxygen coordination. The higher binding energy component is then associated with barium ions having a distorted oxygen neighborhood.

According to Werfel et. al.⁽⁹⁾, the yttrium 3d doublet of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ corresponds to metallic yttrium coordination in the absence of oxygen interaction while the weak shoulders of the doublet components imply the possibility of a second yttrium oxidation state.

The double peak oxygen spectrum obtained by Werfel et. al.⁽⁹⁾ for $\text{YBa}_2\text{Cu}_3\text{O}_7$ was compared to the corresponding spectrum of CuO . The binding energy value for the O 1s line of CuO lies between the values of the two components of that line in the superconductor. These researchers conclude that there are at least three different coordinations associated with oxygen in the superconductor.

Qiu et. al.⁽¹⁰⁾ used XPS spectroscopy based on the use of synchrotron radiation to study the interaction of water with $\text{YBa}_2\text{Cu}_3\text{O}_7$. The oxygen 1s core level was observed at 20 K for a freshly scraped sample both before and after the absorption of a quantity of water. The unreacted surface shows peaks at 529 eV and 531 eV. A peak was generated at 534 eV by water adsorption. The 534 eV peak is identified with molecular water, while the 529 eV and 531 eV peaks are taken to be associated with the oxide O^{2-} structure and the oxygen in a hydroxide OH^- species, respectively. The temperature of the sample is raised to 300 K thus removing the water.

The sample then again displays the oxygen 1s peaks at 529 eV and 531 eV. However, although the sample in its original clean state displayed a 529 eV peak that was approximately six times larger than the 531 eV peak, the 531 eV peak has now become larger than the 529 eV peak. Qui et. al.⁽¹⁰⁾ conclude that the ceramic surface at cryogenic temperatures has been irreversibly altered by water adsorption.

Lengler et. al.⁽¹¹⁾ applied x-ray absorption to the determination of the valence of copper in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. These researchers found that the green phase Y_2BaCuO_5 is a better model for Cu^{2+} than is CuO for comparison with the spectrum of the superconductor because both the green phase and the superconductor have their five nearest oxygens around Cu^{2+} in a square pyramidal configuration. Using Cu_2O , Y_2BaCuO_5 , and KCuO_2 as models for Cu^+ , Cu^{2+} , and Cu^{3+} , respectively, a best fit to the copper K-edge of the superconductor was made, giving that the conductor comprises 0.16 of Cu^+ , 2 of Cu^{2+} , and 0.84 of Cu^{3+} .

In summary, the XPS feature most frequently discussed in the literature is the Cu 2p peak. This is closely followed by the O 1s peak. Based on a comparison of these discussions, the valence state of the Cu, when in a superconducting material, is somewhat unclear. It has been claimed by Ihara et. al.⁽³⁾ for $\text{Sr}_x\text{La}_{2-x}\text{CuO}_{4-x}$ to be monovalent, by Fujimori et. al.⁽⁴⁾ for $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{4-y}$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ to be divalent, by Steiner et. al.⁽⁵⁾ for $\text{YBa}_2\text{Cu}_3\text{O}_7$ to be mainly divalent, by Werfel et. al.⁽⁶⁾ to be a mix of monovalent and divalent, and by Lengler et. al.⁽¹¹⁾ to be a mixture of all three. Our objective will

be to study with non-monochromatic radiation the Cu 2p peak and other features in the XPS spectra and to decide if they can be used to study the reaction of the ceramic superconductors with water.

EXPERIMENTAL PROCEDURE

SAMPLE PREPARATION

Sample preparation started with the mixing of 7.55g of Y_2O_3 , 26.4g of $BaCO_3$, and 16.0g of CuO in powder form with 150 ml of ethanol. The mixture was ball milled for 16 hours and dried in an oven for approximately 4 hours at 100°C. The specimen material was calcined at 860°C to 875°C for 24 hours. Next, the material was ball milled in ethanol for 16 hours and then calcined again at 860°C to 875°C for 24 hours.

After calcining, the material was pressed at 30,000 psi into a disc shape. The specimen was 1 inch in diameter and 3/16 inch thick after pressing. The specimen was heat treated in two stages. The first stage comprised 6 hours at 900°C to 925°C in flowing oxygen. The specimen was then cooled to about 40°C in 16 hours. The second stage comprised 6 hours at 450°C to 500°C in flowing oxygen. When done properly, this procedure results in a sample that is polycrystalline

and by magnet levitation demonstrates superconductivity at the temperature of liquid nitrogen (77 K). For ease of discussion such material will be referred to hereafter as the superconducting sample.

As a first step in using the XPS equipment to study the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with water, it was necessary to ascertain the extent to which the method can tell the difference between a relatively pure form of the single phase $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconducting structure and a sample that is not superconducting due to poor processing or handling. This will aid in separating the spectra features that are due to poor processing and handling from those due to reaction with water vapor. For this reason it was decided that it would be necessary to test a sample that was not the pure phase of $\text{YBa}_2\text{Cu}_3\text{O}_7$. This material was obtained due to an error in the processing, described above, and was a mixture of two phases, $\text{YBa}_2\text{Cu}_3\text{O}_7$ and Y_2BaCuO_5 , as determined by X-ray diffraction. It was not superconducting at the temperature of liquid nitrogen (77 K). For ease of discussion, this material will be referred to hereafter as the non-superconducting sample.

X-RAY PHOTOELECTRON SPECTROSCOPY

Since it is natural to suspect that the reaction of these ceramics with water occurs at surfaces, it might be possible to study this reaction with a surface sensitive method, i.e. XPS. XPS involves exposing the surface of interest to x-rays of a discrete energy. In the Kratos model XSAM 800 surface analyzer used in these experiments

non-monochromatic Al-K α (1486.6 eV) radiation was the source. The interaction of this radiation with the specimen causes the surface to emit electrons with energy characteristic of the atoms and electron orbitals from which they are emitted. The XPS equipment has an electron energy analyzer which measures the kinetic energy of these emitted electrons. This kinetic energy can be related to the binding energy of the electrons. Binding energy values are most frequently used and are the ones that we report.

Since the kinetic energy of electrons is being measured, ultra-high vacuum conditions (UHV) are required in the sample analysis chamber. Without the UHV conditions the electrons would be scattered by the gas molecules before reaching the analyzer. In addition, the UHV keeps the specimen surface from being contaminated with ambient gases during the analysis. The surface sensitivity of the XPS method arises from the fact that it measures the energy of emitted electrons. These electrons have a very short mean-free path (5 to 10 x 10⁻¹⁰ m) in solids. Consequently, these emitted electrons represent elements present in the outer layer or several atomic layers below the surface.

The data was acquired with fixed analyzer transmission, low analyzer magnification, low resolution, a start energy for the scans of 1000 eV, a step size per channel of 0.25 eV, and a dwell time per channel of 0.4 second. All XPS peaks were referenced to the adventitious carbon 1s peak of 284.6 eV. The analyzer was calibrated to the gold 4f_{7/2} peak at 83.8 eV and the cobalt 2p_{3/2} peak at 778 eV

with an error of ± 0.25 eV. Combined with an error of ± 0.25 eV in referencing all the peaks to that of adventitious carbon, the overall error in peak location is ± 0.5 eV.

The spectra were acquired for the specimen surfaces after 5 minutes of argon ion bombardment with the ion gun attached to the analyzer chamber. The ion gun allows an accelerated ionized beam of argon atoms to impinge onto the specimen surface. By a collision process, this strips off the surface layers. Typical ion gun parameters were a beam voltage of 4.5 kilovolts, an emission of 25 milliamps, a pressure in the gun of 20×10^{-3} Pa, and with the beam rastered over the entire surface. The specimens measured approximately 9 mm in diameter and were held to the specimen manipulator by conductive tape.

A computerized peak synthesis method was used to aid in determining whether various peaks in the XPS spectra were due to the overlapping of peaks from different chemical or valence states of an element. The overlap results because the widths of the photoelectron peaks are often larger than the difference in the core binding energies of the different chemical states. The method synthesizes a composite peak from information provided by the operator as to the location, the FWHM, intensity, and shape (Gaussian in this work) of suspect peaks hidden in the actual spectra. This composite spectra can then be compared to and overlaid onto the actual spectra from which the background has been removed. The operator supplied

values can then be varied as required to improve the degree of fit of the synthesized peak to the actual peak.

RESULTS AND DISCUSSION

The XPS spectra for the Cu $2p_{3/2}$ peak of the superconducting specimen is shown Figure 1(a). The peak is located at 933.2 eV, which is close to that for Cu $2p_{3/2}$ peak as found for CuO⁽¹²⁾. To study whether the peak from the superconducting specimen might be a convolution of more than one peak representing mixed valent states for Cu, it was decided to perform a three (Figure 1(b)) and a two peak (Figure 2(a)) synthesis of the primary peak. There were no outstanding features in either of these synthesized peaks that suggest it would be more appropriate to choose one over the other. Steiner *et. al.*⁽⁹⁾ have given the Cu⁺¹, Cu⁺², and Cu⁺³ peaks as 932.7, 933.6, and 934.7 eV, respectively, and we have also used these three peak locations. However, Steiner *et. al.*⁽⁹⁾ found that divalent Cu should have a FWHM that is twice that of either monovalent or divalent copper and we could not get a reasonable peak synthesis with such a relationship. In fact the peak in Figure 1(a) appears to be almost all divalent copper. Consequently, while it might be possible to claim that the three peak synthesis in Figure 1(b) shows evidence of Cu in a +3 valent state, if compared to the work of Werfel, *et. al.*⁽⁹⁾, it is believed that there is not enough of a

difference between the peak in Figure 1(a) and that reported for $\text{CuO}^{(12)}$ to support such a conclusion.

The XPS spectra for the $\text{Cu } 2p_{3/2}$ peak of the non-superconducting specimen is shown in Figure 3(a). The peak is located at 932.9 eV. Taking into account the experimental error of our equipment, this peak is close to that for Cu as in $\text{CuO}^{(12)}$. A three peak synthesis was also made of this primary peak (Figure 3(b)). The locations of the peaks were 932.2, 932.9, and 934.

The $\text{Cu } 2p_{3/2}$ peaks are somewhat different for the material in its two conditions (Figures 1(a) and 3(a)); however, they are not different enough from each other or CuO to be conclusive by themselves in discriminating a properly processed sample of $\text{YBa}_2\text{Cu}_3\text{O}_7$ from a poorly processed sample.

Figure 4(a) and 4(b) show the original and two peak synthesis of the yttrium 3d peak for the superconducting sample. In general, the Y 3d peak is actually comprised of the $\text{Y } 3d_{5/2}$ and $\text{Y } 3d_{3/2}$ peaks with these peaks being located at 156.40 eV and 158.15 eV, respectively, according to standard tables⁽¹²⁾. The Y 3d peak of our spectra, (Figure 4), at 156.65 eV decomposes into a $\text{Y } 3d_{5/2}$ peak at 156.25 eV and a $\text{Y } 3d_{3/2}$ peak at 158.05 eV.

Figures 5(a) and 5(b) show the original and two peak synthesis of the Y 3d peak for the non-superconducting sample. This Y 3d peak,

found at 159.2 eV, decomposes into a Y $3d_{5/2}$ peak at 155.7 eV and a Y $3d_{3/2}$ peak at 157.6.

The non-superconducting sample (Figure 5) shows from visual inspection a less pronounced distinction between Y $3d_{5/2}$ and Y $3d_{3/2}$ peaks than for the superconducting sample (Figure 4).

In Dauth et. al.⁽⁶⁾ the two-peak structure of the Y 3d core level spin-orbit doublet shows more clearly than it shows in the case of the superconducting sample of this investigation. Referring to the investigation of Iqbal et. al.⁽¹³⁾, it is noted that the double peak structure for the Y 3d peak for green Y_2BaCuO_5 is hardly noticeable compared to the corresponding peak for $YBa_2Cu_3O_{7-x}$ produced by annealing in oxygen. The work of Iqbal et. al.⁽¹³⁾, may indicate that the failure of the non-superconducting sample to manifest any signs of superconductivity at 77 K arises, at least in part, from the presence of Y_2BaCuO_5 . Thus, it may be possible to use the Y 3d peak to distinguish a properly processed sample of $YBa_2Cu_3O_7$ from a poorly processed sample.

Figures 6(a) and 6(b) show the original and the two peak synthesis of the barium $3d_{5/2}$ peak for the superconducting sample.

Iqbal et. al.⁽¹³⁾, find that the $3d_{5/2}$ barium peak for $YBa_2Cu_3O_{7-x}$ shows signs of being comprised of two peaks. Although the Ba $3d_{5/2}$ peak in Figures 6 can be synthesized from two peaks, there are no visible features that would indicate that it was made up of two peaks.

Figures 7(a) and 7(b) show the original and the two peak synthesis for the barium 3d_{5/2} peak for the non-superconducting sample. There does not appear to be any significant difference between the barium peaks for this specimen (Figure 7) and the corresponding peaks for the superconducting specimen (Figure 6). This means that the Ba 3d_{5/2} peak will be difficult to use for distinguishing these materials.

Figure 8 shows the oxygen 1s peak for the superconducting sample. On the high energy side of the peak there is a noticeable change in slope which indicates the presence of two overlapping peaks. Using two peaks to synthesize the experimentally observed peak at 528.95 eV results in locating them at 528.55 and 530.65 eV.

While there are no obvious changes in slope on the sides of the oxygen 1s peak for the non-superconducting sample (Figure 9), the experimental peak is wide enough (approximately 6eV) to indicate that it is actually a composite of two peaks. Using two peaks to synthesize the actual spectra results in locating them at 528.9 and 531.2 eV. Both spectra (Figures 8 and 9) indicate the presence of oxygen in two states. Qui *et. al.*⁽¹⁰⁾ say that the two peaks can be associated with oxide in an O²⁻ structure and a peroxide structure. There has been a change in the proportion two peaks used in the synthesis of Figures 8 and 9. This could prove to be a useful feature in discriminating these materials or it could be a normal variation for this class of materials. Studies are in progress of the other stable phases in the Y-Ba-Cu-O system (such as BaCuO₂, Y₂Cu₂O₅, and

Y_2BaCuO_5) to clarify the source of these two peaks for oxygen. It will be best to wait for the completion of those efforts before attributing these peaks to some sort of differing oxygen states in the $YBa_2Cu_3O_7$ phase itself.

SUMMARY

Core-level XPS spectra for superconducting ($YBa_2Cu_3O_7$) and non-superconducting ($YBa_2Cu_3O_7 + Y_2BaCuO_5$) samples in the Y-Ba-Cu-O system were acquired in this investigation. Differences in the spectra for the Y 3d and O 1s peaks were found that might prove useful in distinguishing these two materials and studying the reaction of $YBa_2Cu_3O_7$ with water. Core-level XPS spectra will be acquired for other stable phases in the Y-Ba-Cu-O system (such as $BaCuO_2$, $Y_2Cu_2O_5$, and Y_2BaCuO_5) to continue building the basis from which the reaction of $YBa_2Cu_3O_7$ with water can be studied.

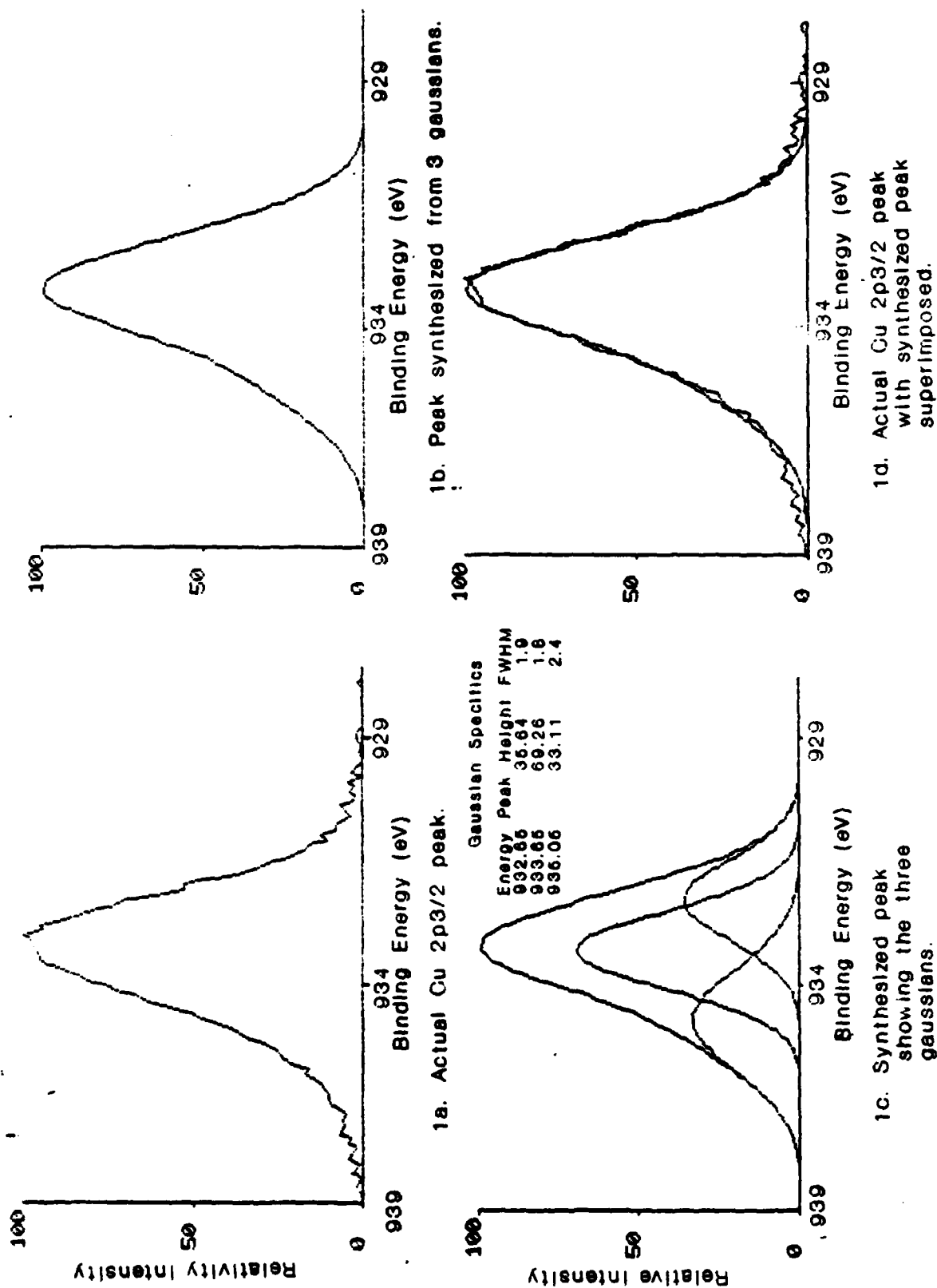


Fig. 1. Cu 2p 3/2 peak synthesis using three gaussians for the superconducting sample.

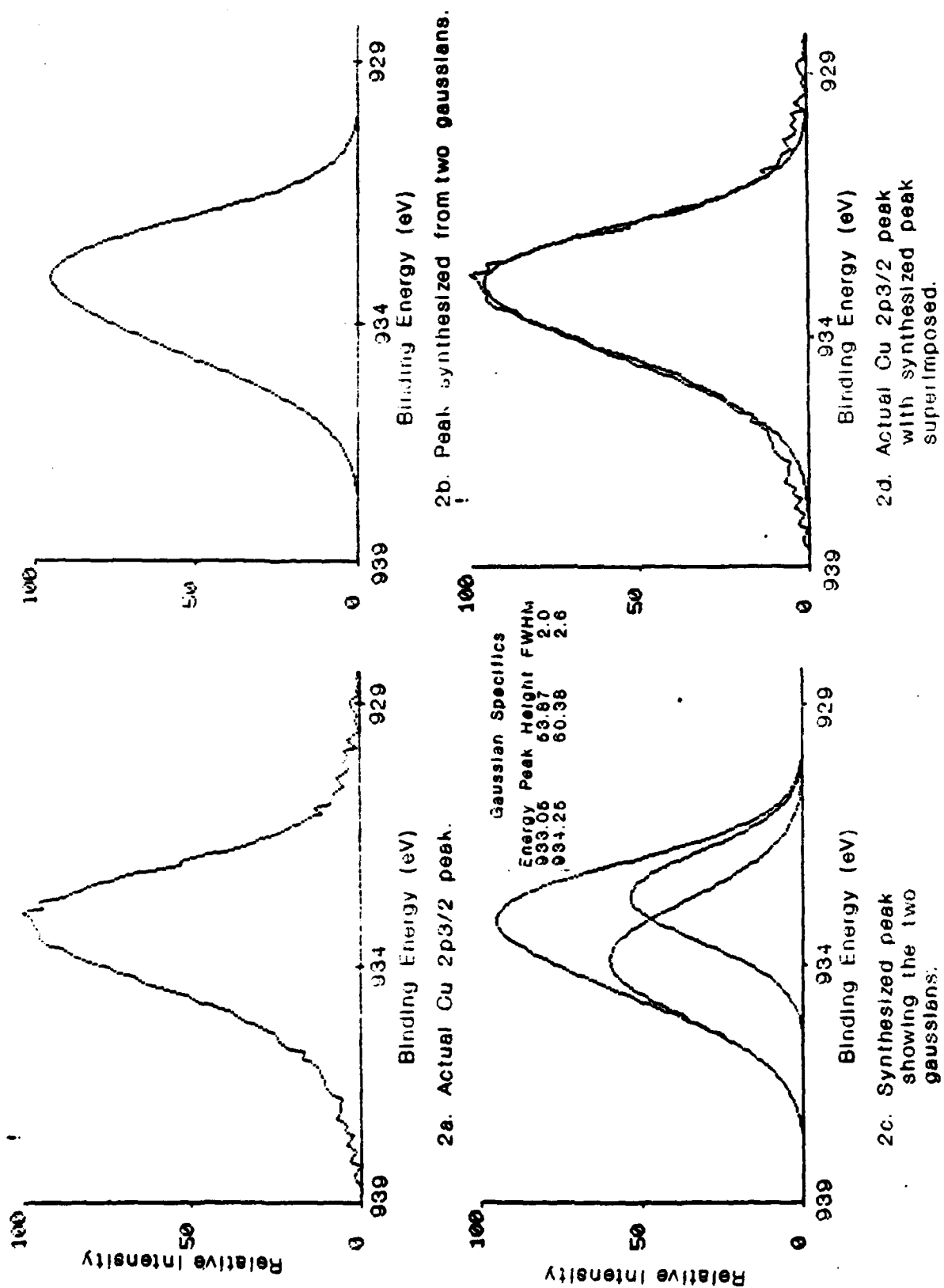


Fig. 2. Cu 2p $3/2$ peak synthesis using two gaussians for the superconducting sample.

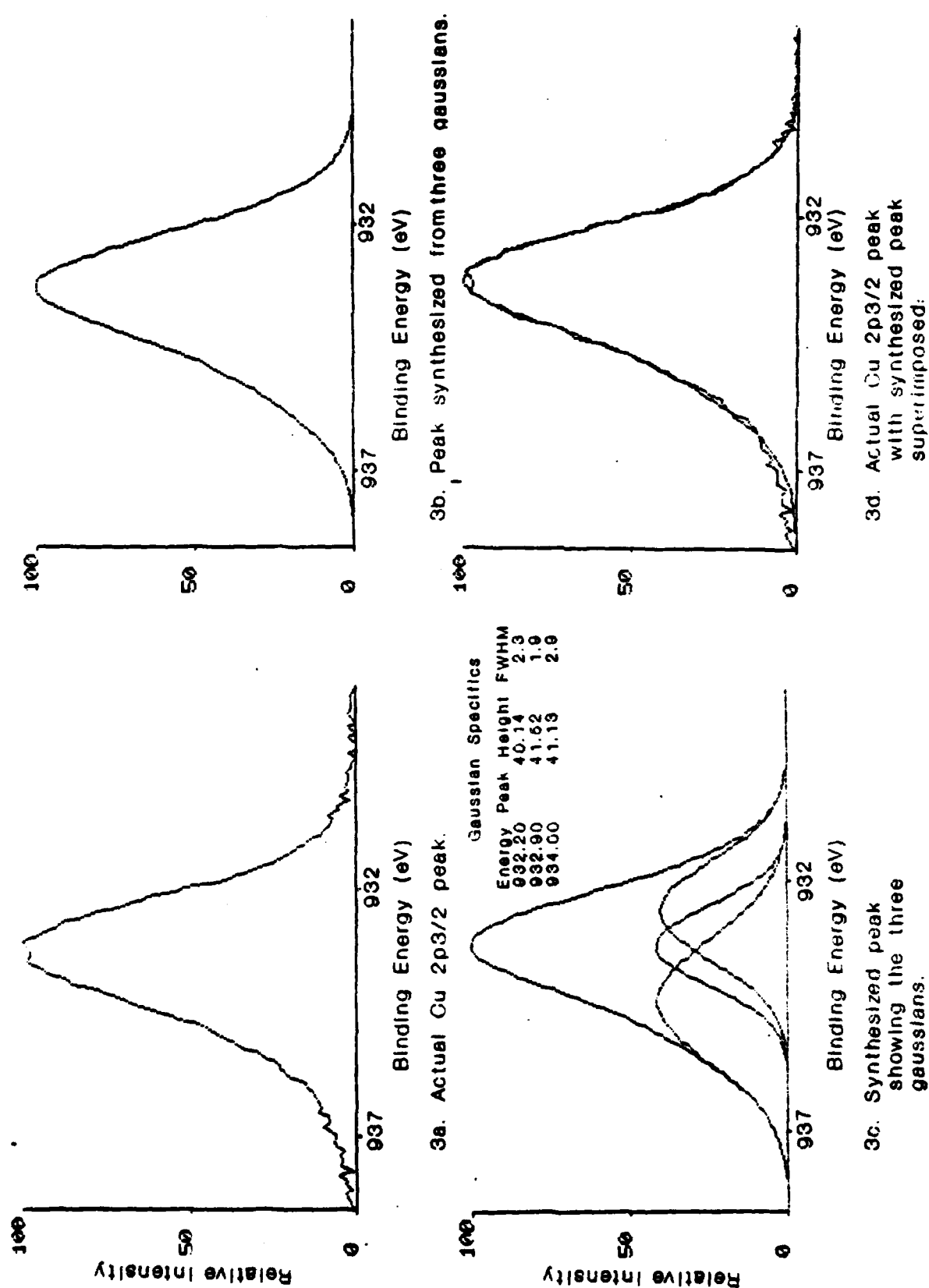
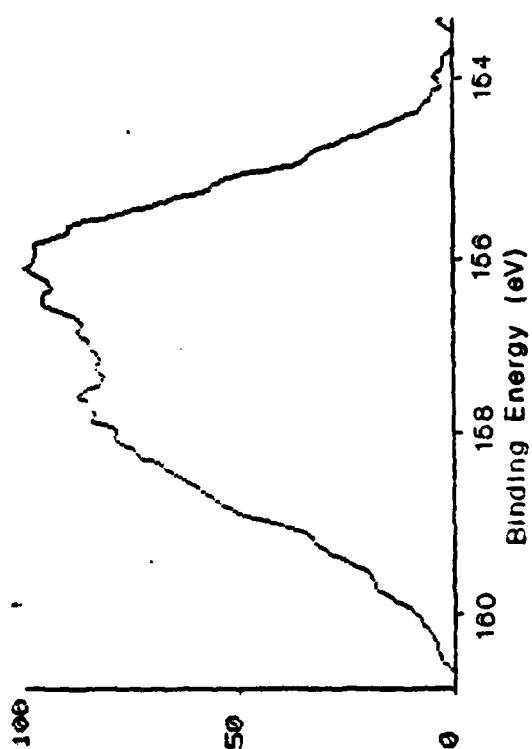
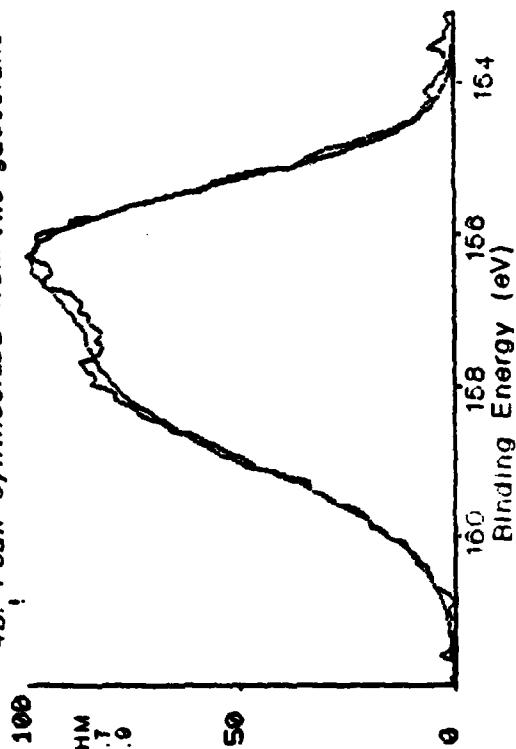


Fig. 3. Cu 2p 3/2 peak synthesis using three gaussians for the "non-superconducting" sample.



4b. Peak synthesized from two gaussians



4c. Synthesized peak showing the two gaussians.

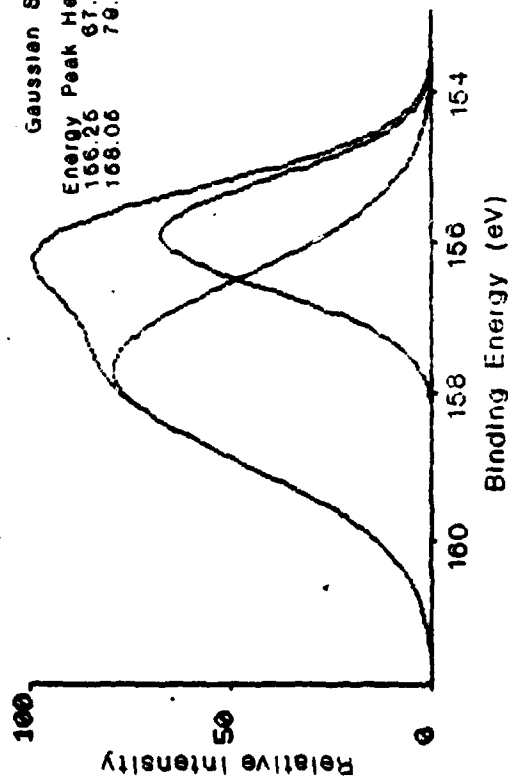
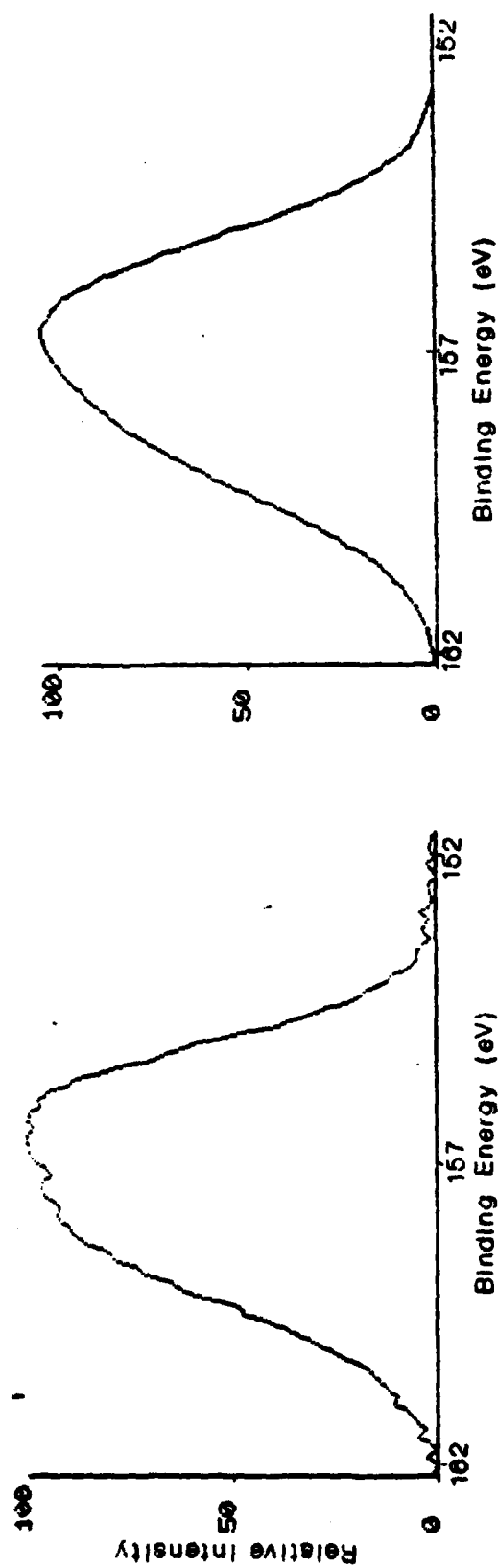
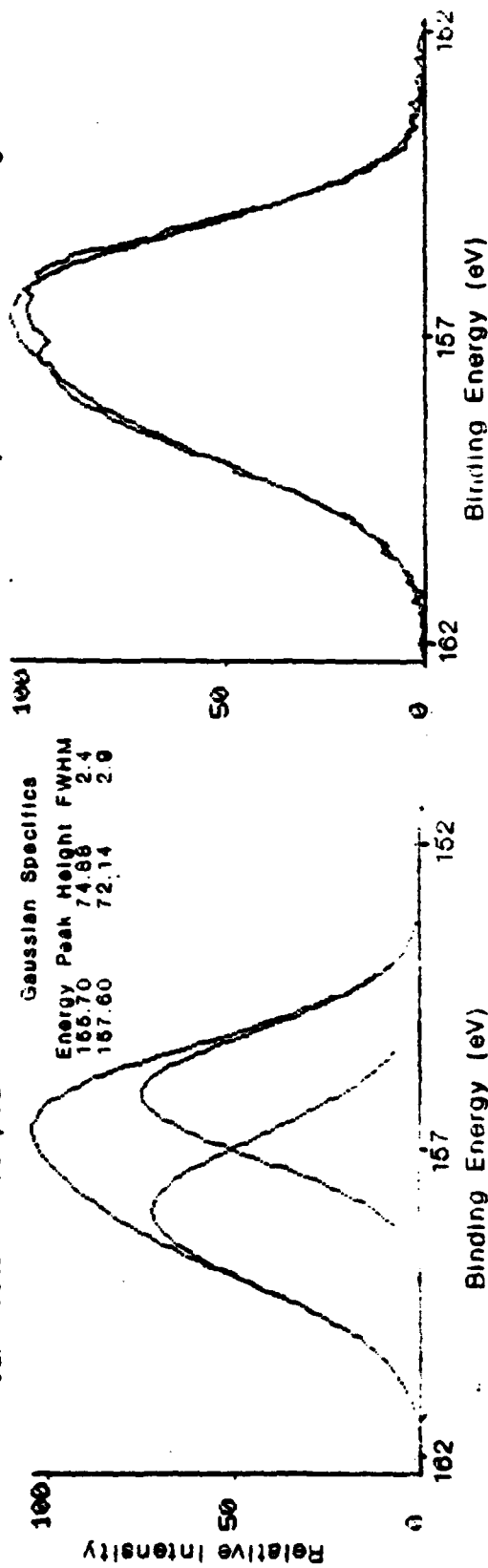


Fig. 4. Y 3d peak synthesis using three gaussians for the superconducting sample.



5b. Peak synthesized from two gaussians



5d. Actual Y 3d peak with synthesized peak superimposed.

Gaussian Specifics

Energy	Peak Height	FWHM
166.70	74.88	2.4
157.60	72.14	2.0

5c. Synthesized peak showing the two gaussians.

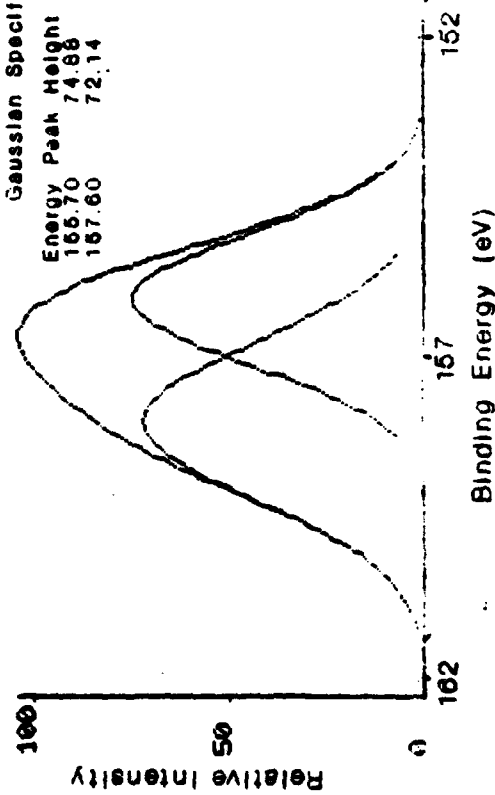
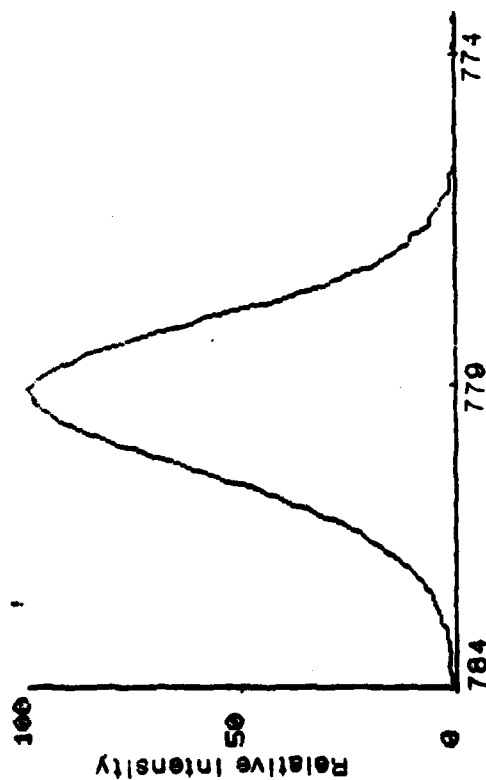
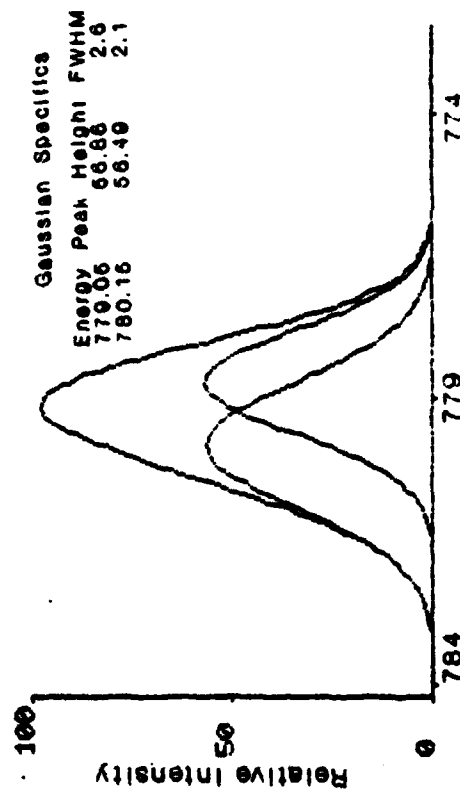


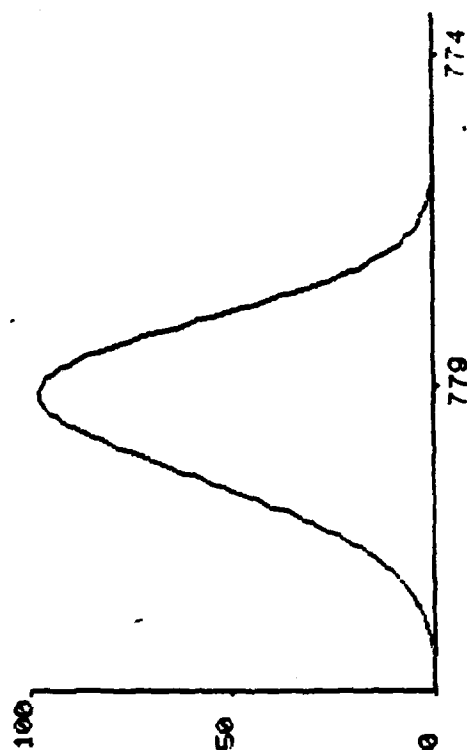
Fig. 5. Y 3d peak synthesis using three gaussians for the "non-superconducting" sample.



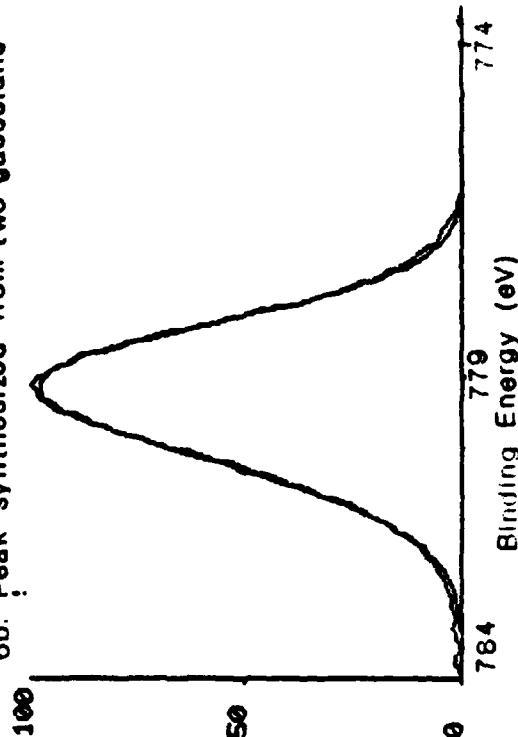
6a. Actual Ba 3d 5/2 peak.



6c. Synthesized peak showing the two gaussians.



6b. Peak synthesized from two gaussians



6d. Actual Ba 3d 5/2 peak with synthesized peak superimposed.

Fig. 6. Ba 3d 5/2 peak synthesis using two gaussians for the superconducting sample

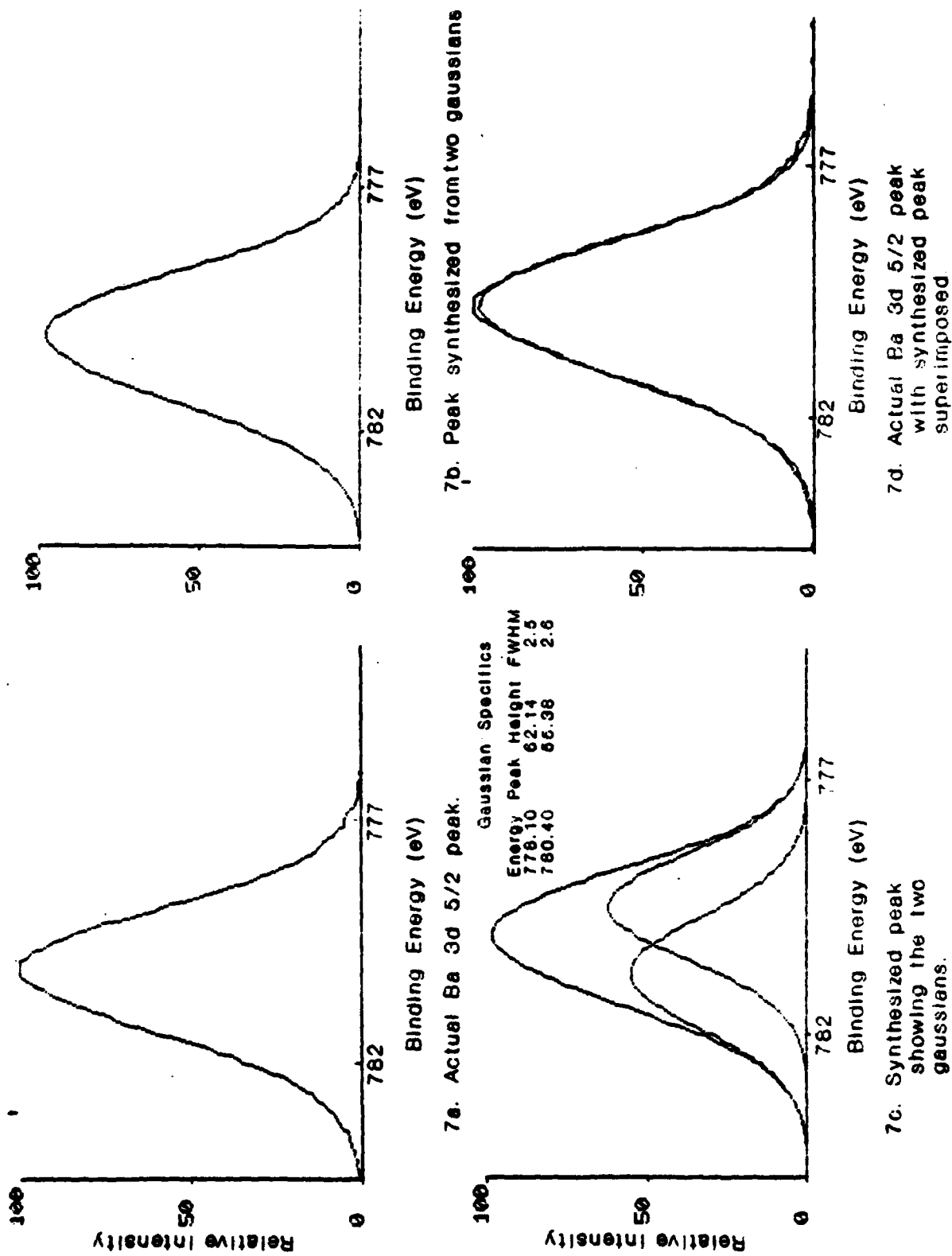


Fig. 7. Ba 3d 5/2 peak synthesis using two gaussians for the "non-superconducting sample".

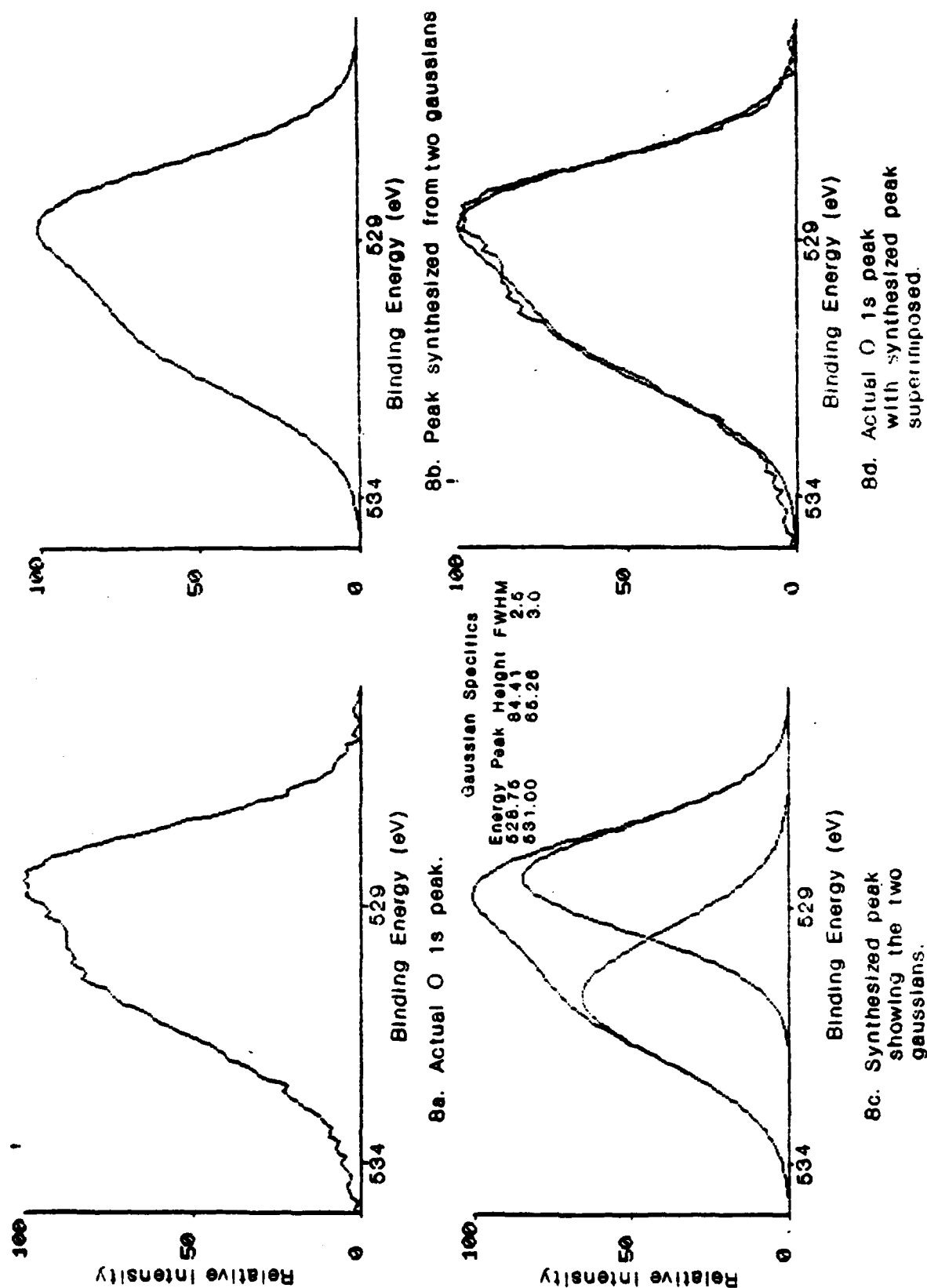


Fig. 8. O 1s peak synthesis using two gaussians for the superconducting sample.

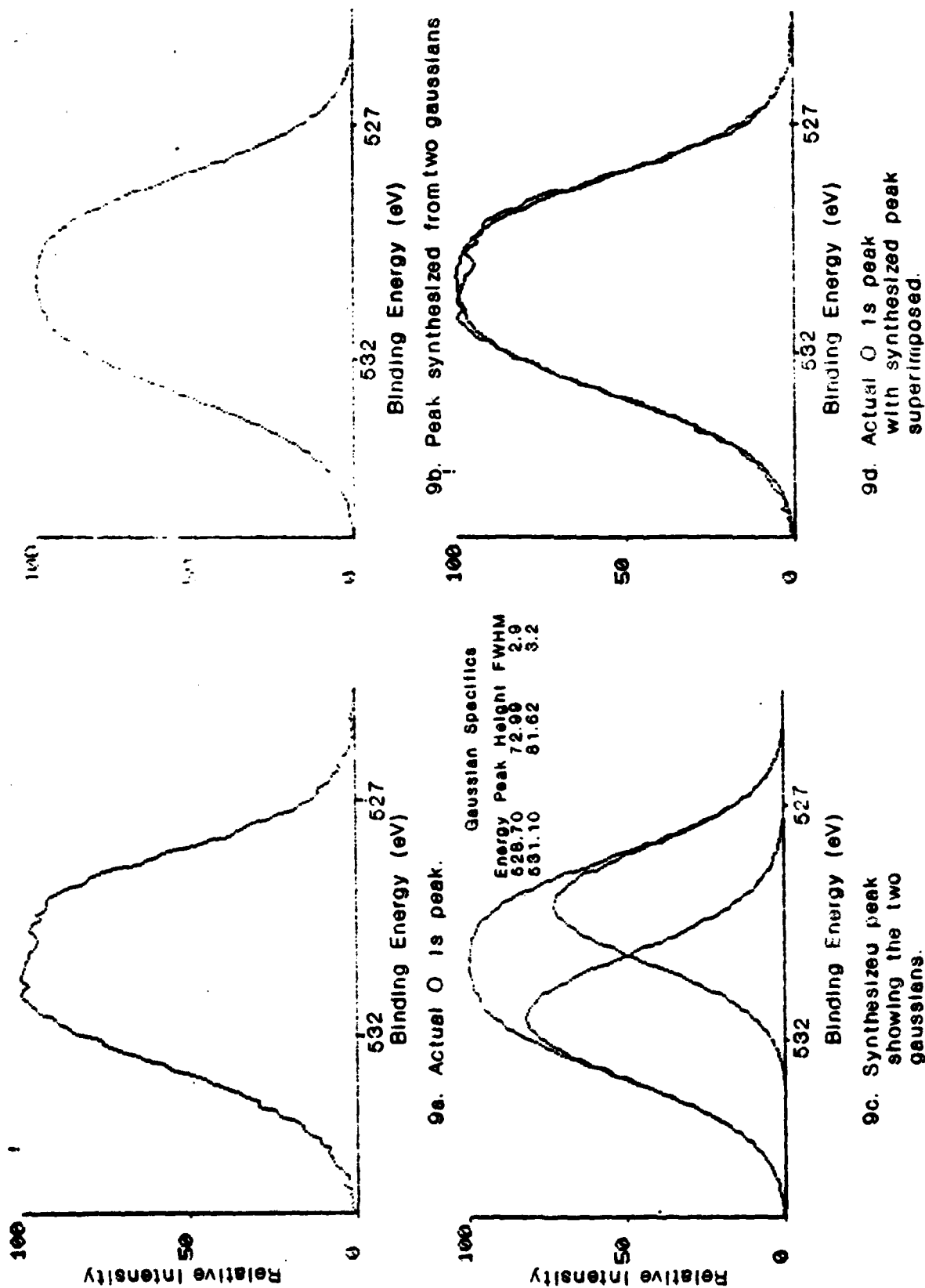


Fig. 9. O 1s peak synthesis using two gaussians for the "non-superconducting" sample.

REFERENCES

1. Wu, M.K., J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Gao, J.I. Huang, Y.Q. Wang, and C.W. Chu, Physical Review Letters, 1987, vol. 58, 908.
2. Carlson, Thomas A., Photoelectron and Auger Spectroscopy, Plenum Press, New York, (1975).
3. Ihara, H., M. Hirabayashi, N. Terada, Y. Kimura, K. Senzaki and M. Tokumoto, "Superconductivity and Electronic Structure of $\text{Sr}_{1-x}\text{La}_x\text{CuO}_{4-y}$ Prepared Under Reducing Condition," Japanese Journal of Applied Physics, vol. 26, no. 4, pp. L463-L465, (April 1987).
4. Fujimori, A., T. Muromachi, Y. Uchida, and B. Okai, "Spectroscopic Evidence For Strongly Correlated Electronic States in La-Sr-Cu and Y-Ba-Cu oxides," Physical Review B, vol. 35, no. 6, pp. 8814-8817, (1 June 1987)
5. Jenny, H., B. Walz, G. Leeman, V. Geiser, S. Jost, T. Frey, and H. J. Guntherodt, "Magnetic and Electronic Properties of M-Ba-Cu-O (M = Y, Er, Eu)," J. Mater-Res., vol. 2, no. 6, pp. 775-778, (Nov/Dec 1987).

6. Dauth, B., T. Kachel, P. Sen, K. Fischer, and M. Campagna, "Valence Fluctuations and Oxygen Dimerization in High-Temperature Superconductors from X-ray Photoemission Spectroscopy," Z. Phys. B Condensed Matter, vol. 68, pp. 407-410., (1987).
7. Ramaker, D.E., N.H. Turner, J.S. Murday, L.E. Toth, M. Osofsky and F.L. Hutson, "Observed Trends in The X-ray Photoelectron and Auger Spectra of High-Temperature Superconductors," Physical Review B, vol. 36, no. 10, pp. 5672-5675, (1 Oct. 1983).
8. Steiner, P., V. Kinsinger, I. Sander, B. Siegwart, S. Heifner, C. Politis, R. Hoppe, and H.P. Miller, "The Cu Valence in the High Tc Superconductors and in Monovalent, Divalent and Trivalent Copper Oxides Determined from XPS Core Level Spectroscopy," J. Phys. B. Condensed Matter, vol. 67, pp. 497-502, (1987).
9. Werfel, F., M. Heinonen, and E. Suoninen, "Oxidation States of Cu, Ba and Y in Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$," J. Phys. B Condensed Matter, vol. 70, pp. 317-322, (1988).
10. Qiu, S.L., M.W. Ruckman, N.B. Brookes, P.D. Johnson, J. Chen, C.L. Ling, and Myron Strongin, "Interaction of H_2O with a High-Temperature Superconductor", Physical Review B, vol. 37, no. 7, pp. 3747-3750, (1 Mar 1988).

11. Lengeler, B., M. Wilhelm, B. Jobst, W. Schwaen, B. Seebacker and U. Hillebrecht, "The Valence of Copper in $\text{YBa}_2\text{Cu}_3\text{O}_{6-x}$ -- An X-ray Absorption Study," Solid State Communications, vol. 65, no. 12, pp. 1545-1548, (1988).
12. Wagner, C.D., W.M. Riggs, L.E. Davis, J.F. Moulder, and G.E. Muilenberg, Eds., Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden-Prairie, Minn., (1979).
13. Iqbal, J., E. Leone, R. Chin, A.J. Signorelli, A. Bose, and E. Eckhardt, "X-ray Photoemission Spectroscopy of the 90 K Superconductor $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$," J. Matr. Res., vol. 2, no. 6, pp. 768-774, (Nov/Dec 1983).

INITIAL DISTRIBUTION

Copies

12 DTIC

CENTER DISTRIBUTION

Copies	Code	Name
1	0113	Lukens
1	28	Wacker
1	2801	Crisci
1	281	
1	2812	
15	2812	Aprigliano
10	5211.1	
1	522.1	TIC (C)
1	522.2	TIC (A)
1	5231	Office
		Services